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Electronic States of Heavily Doped Molecular Crystals—Naphthalene. II. Experimental*

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The energy states and optical spectra of heavily doped mixed crystals are investigated. Studies are made for the following binary systems: (1) naphthalene-h_8 and -d_8, (2) naphthalene-h_8 and -αd_4, and (3) naphthalene-h_8 and -βd_1, corresponding to strong, medium, and weak perturbations, respectively. In addition to ordinary absorption spectra at 4°K, band-to-band transitions at both 4 and 77°K are also analyzed with emphasis on their relations to cooperative excitation and over-all density-of-states functions for mixed crystals. It is found that the theoretical calculations presented in a previous paper agree generally with experiments except for cluster states observed in system (1) at lower guest concentrations. These features are discussed semiquantitatively. As to the intermolecular interaction parameters, it is found that experimental results compare favorably with calculations based on experimental density-of-states functions but not with those based on octopole interactions or charge-transfer interactions. Previous experimental results of Sheka and the theoretical model of Broude and Rashba are also compared with present investigations.

I. INTRODUCTION

Isotopically mixed crystals are widely used as convenient systems for the study of elementary excitations in molecular aggregates. A study of the mixed crystal problem not only provides information about the mixed crystal itself but it also provides information concerning the pure crystal. The chief advantages of studying isotopic mixed crystal systems are: (1) The intermolecular interactions can be assumed, to a large extent, to be invariant upon isotopic substitutions; (2) the "guest" molecules enter substitutionally into the "host" lattice without disturbing the crystal structure; (3) the entire concentration range 0%–100% is available; and (4) relative guest–host excitation energies are variable simply by making different kinds of isotopic substitution.

In the discussion of mixed crystals, two cases can be distinguished: (1) the dilute mixed crystal, and (2) the heavily doped mixed crystal. In the former case, the energy level of the guest is governed predominantly by quasiresonance interactions[1] with the host (the host levels are essentially unchanged). In the latter case, the energy spectrum of the entire system is now determined by both the resonance interactions between like molecules and the quasiresonance interactions between unlike molecules. Further complications due to the random distributions of the two components also add to the complexity of the latter problem.

In the first paper (I) of this series,[2] we presented a Green's function formulation for the electronic states of heavily doped molecular crystals with multiple-branched exciton bands. By assuming that the factor-group operations can be applied to all the $\mathbf{k}$ states,[3] we have been able to do the statistical averaging exactly. It was also shown that in the first approximation, the density-of-states function and optical spectrum of a mixed crystal are completely determined by the density-of-states function of the pure crystal and the excitation energy separation between the two components. Model calculations on the electronic states of the naphthalene mixed crystals, based on both the experimental density-of-states function of Colson *et al.*[4] and that of the octopole model of Craig and Walmsley,[5] were also presented. The present experimental investigations are aimed at a critical evaluation of the theory. Furthermore, wherever discrepancies are observed, we hope to present some experimental facts that might suggest directions for the future improvement in the theory of disordered solids.

Although the optical spectra of some naphthalene mixed crystals have been investigated by Sheka[6] at 20°K, he did not use weighed samples. Rather, the approximate formula of Broude and Rashba[7] was used to fit the spectra and to determine the compositions. When additional experimental data at lower temperatures with weighed samples were gathered in the present study, some disagreements with Sheka's results were noted and some new features observed. Such disagreements will be discussed here. In addition, the present study was carried out to include systems with smaller energy "gaps" and to undertake a more thorough study of the vibronic band-to-band transitions at different temperatures.

II. EXPERIMENTAL

The absorption spectra of napthalene mixed crystals were taken at 4.2°K using an 800-W Hanovia high-pressure Xenon lamp and a 2-m Czerny–Turner spectrograph in third order. The dispersion on the plate is about 2.4 Å/mm. An aqueous solution filter of cobalt chloride in a 5-cm quartz cell and a Corning 9863 glass filter were used to eliminate overlapping orders. The fluorescence spectra at 4.2°K were taken photographically with the same spectrograph. Front surface excitation was employed using a P.E.K. 200-W mercury lamp with air cooling. A small 0.25-m Bausch & Lomb high-intensity monochromator was used in addition to a $CoCl_2$ solution filter to provide a narrow band at 3100 Å for excitation. A Corning 9863 filter (and/or 5840 filter) was placed in front of the slit to eliminate the

phosphorescence. With a typical slit setting of 30 μ, the exposure times ranged from 30 min to 1 h. At liquid-nitrogen temperature, the fluorescence was found to be considerably weakened. For the fluorescence experiments, the same optical arrangement as above was employed, except that a large Osram XBO-6500 lamp and a 1.8-m Jarrell–Ash photoelectric spectrometer were used for excitation and dispersion. An EMI 6256S photomultiplier selected for low dark current and installed in a light-tight housing suitable for dry-ice cooling was used as a detection probe.

The spectral line positions on a photographic plate were measured relative to the standard emission of an iron–neon hollow cathode on a Jarrell–Ash high-precision recording microphotometer (Model No. 23-500). When the photoelectric method was used, the wavelengths were measured by calibrating the spectrometer readings with known mercury emission lines. The measured wavelengths were then converted to wavenumbers and corrected for vacuum using Kayser's *Tabelle der Schwingungszahlen.*

Eastman Kodak recrystallized naphthalene was purified with zone refining and potassium fusion.[8] Deuterium-substituted naphthalenes (naphthalene-d_8, naphthalene-αd_4, naphthalene-βd_1) were all obtained from Merck, Sharp & Dohme of Canada Ltd. and subjected to the same purification processes. The purified substances were removed from the vacuum-sealed tube and exposed to air temporarily while being weighed and mixed. To minimize air contamination, the following procedures were followed to introduce the weighed samples into the vacuum line: (1) The vacuum system was evacuated to a pressure of 10^{-6}–10^{-7} torr. (2) The system was filled with helium gas and maintained at a pressure slightly above atmospheric. (3) The system was opened with a torch and the sample was introduced. Since the system had a positive pressure, no air could diffuse into the system during this operation. (4) The helium pressure was reduced to nearly amospheric and the system was sealed again. (5) The sample inside the vacuum line was cooled to 77°K while helium gas was pumped away. (6) The mixture was then transferred *in vacuo* to a crystal-growing quartz cell that was subsequently pulled from the vacuum line at a pressure of 10^{-6}–10^{-7} torr. To assure good mixing, the sample cell was placed in an oven maintained at a temperature slightly above the melting point of naphthalene (80.2°C) for 1 h, then crystals were grown inside the quartz cell. Since the crystals obtained were apparently not single, no polarization measurements were attempted.

The thickness of the sample cells ranged from 10 to 100 μ. Normally, the thicker cells were used for preparations composed predominantly of one component in order to observe weaker absorptions due to the minor component, and the thinner cells were used for approximately equimolecular mixtures. Some crystals did not have uniform thickness over the whole window area, and it was necessary to take absorption spectra at different locations to select an optimum thickness.

III. RESULTS AND DISCUSSION

A. Absorption

1. Naphthalene-h_8 and Naphthalene-d_8

This system was investigated by Sheka[6] at 20°K using tiny single crystals ($\sim$1 mg) with thicknesses ranging from 10–0.3 μ. From the experimental results, Sheka concluded that: (a) At low concentrations ($<10\%$), the guest level appeared as an unsplit level with mixed polarization. At slightly higher concentrations ($\gtrsim 10\%$), two levels with unique polarizations were observed. The splitting between the two was found to increase gradually with increasing concentration until it reached the full Davydov splitting characteristic of the pure crystal. (b) Due to exciton interactions Beer's law is violated. The absorption attributable to each component is no longer proportional to its concentration. Furthermore, the outer bands (i.e., the **ac** component of naphthalene-h_8 absorption and the

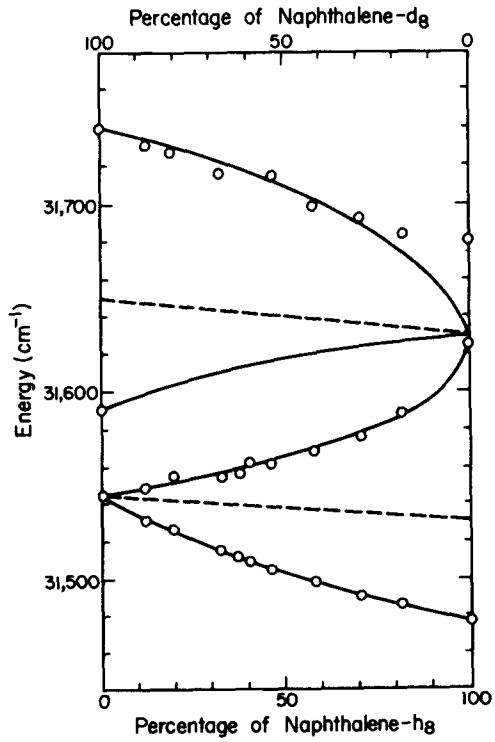

FIG. 1. The positions of Davydov components vs concentration for naphthalene-h_8 and -d_8 mixed crystals as reported by Sheka.[6] The solid curves are calculated by Sheka based on the model of Broude and Rashba.[7] The dotted lines represent their assumed concentration-dependent band center terms.

b component of the naphthalene-d_8 absorption) are enhanced while the inner bands are weakened. The behavior of these features observed by Sheka is qualitatively in agreement with the approximate model of Broude and Rashba.[7] In Fig. 1 the experimental results of Sheka and the theoretical curve of Broude and Rashba are reproduced. Although the agreement appears to be satisfactory, it is for the most part superficial as can be concluded from the following points:

(1) The ideal mixed crystal level (or the center of the exciton band), which is the quantity required in applying the formulas of Broude and Rashba, was determined from Broude's[9] method of vibronic analysis. This method has been criticized by Nieman and Robinson[10] in the past and its limitations were recently re-examined by Colson.[11] Unless it is critically used, this method is likely to yield incorrect values. In this particular instance, the ideal mixed-crystal level was determined by Broude's method to be 31 530 cm^{-1} for the h_8 pure crystal. This is even lower than the isolated impurity level of h_8 in d_8 at 31 542 cm^{-1}. On the other hand, reliable data obtained from hot band spectroscopy place the ideal mixed-crystal level at 31 556 cm^{-1}.[1a,3]

(2) To circumvent the difficulties in the method of Broude and Rashba in the limits of vanishing concentration of each component, $C_{h_8}\rightarrow 0$ and $C_{d_8}\rightarrow 0$, Sheka apparently assumed that ϵ_{h_8} and ϵ_{d_8} had a linear dependence on the concentration. That is,

$$\epsilon_{h_8}=\epsilon_{h_8}{}^{i}-C_{h_8}(\epsilon_{h_8}{}^{i}-\epsilon_{h_8}{}^{0}) \qquad (1)$$

and

$$\epsilon_{d_8}=\epsilon_{d_8}{}^{0}-C_{h_8}(\epsilon_{h_8}{}^{i}-\epsilon_{h_8}{}^{0}), \qquad (2)$$

where $\epsilon_{h_8}{}^{0}$ and $\epsilon_{d_8}{}^{0}$ are the band centers of pure crystalline naphthalene-h_8 and -d_8, respectively. $\epsilon_{h_8}{}^{i}$ corresponds to the experimental value of the isolated impurity level of naphthalene-h_8 in -d_8. Equation (1) was designed such that at $C_{h_8}=0$, $\epsilon_{h_8}=\epsilon_{h_8}{}^{i}$. Since the model of Broude and Rashba did not take into account the quasiresonance interactions, Sheka must have inferred from his erroneous value of $\epsilon_{h_8}{}^{0}$ that the shift from $\epsilon_{h_8}{}^{0}$ to $\epsilon_{h_8}{}^{i}$ was due to the change in the static environmental perturbations (i.e., a change in the D term in the conventional Davydov exciton theory). In order to be self-consistent, Eq. (2) was devised. Although this procedure enabled Sheka to obtain better agreement between theory and experiment for the h_8 bands, it inevitably added to the discrepancies involving the d_8 bands. There appears to be ample experimental evidence to support the assumption that the D term for the naphthalenes is invariant with respect to isotopic substitution. In fact, using the correct values of the ideal mixed-crystal levels, both Hanson *et al.*[1a] and Sommer and Jortner[1b] have satisfactorily interpreted the isolated impurity levels of various naphthalene

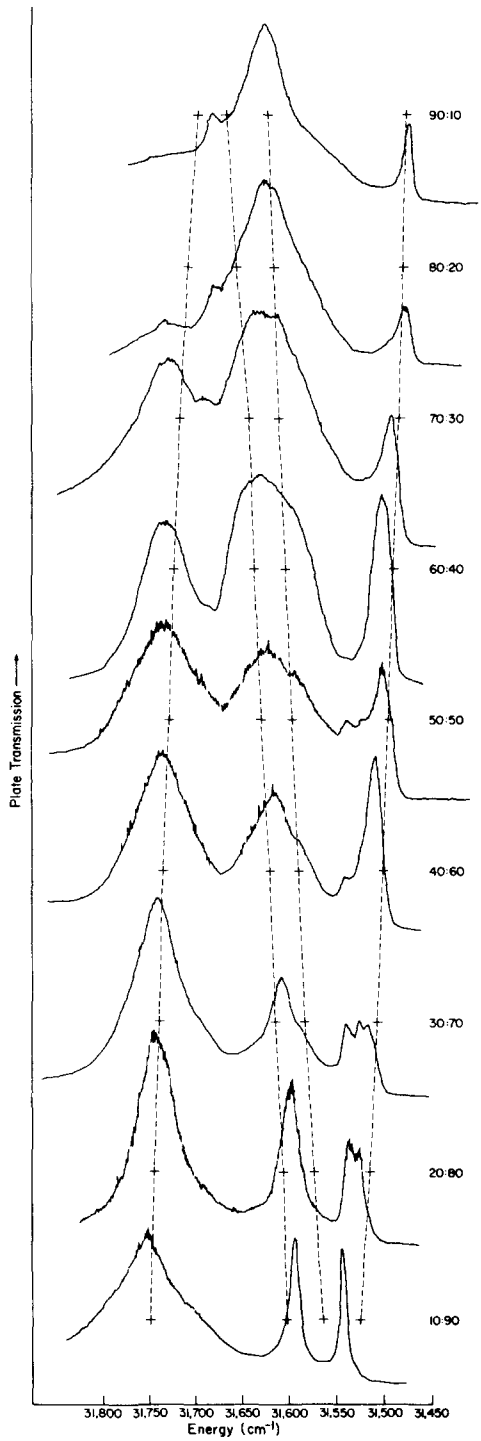

FIG. 2. The absorption spectra of naphthalene-h_8 and -d_8 mixed crystals obtained in this work. The calculated positions of the Davydov components are shown by daggers. The ratios correspond to naphthalene-h_8:naphthalene-d_8 given to the closest 10%(±2%). Some of the weak absorptions due to cluster states are lost in the microphotometer tracing. See text.

mixed crystals in terms of the quasiresonance shift, assuming that no change in the D term was involved.

(3) Sheka did not use weighed samples because of difficulties involved in weighing small quantities of his preparations. Rather he determined the compositions of mixed crystals by fitting the experimental values of the long-wavelength absorptions (**ac** component of the absorption) with the theoretical curve obtained from the above procedures. This introduced more uncertainties into his experimental results. In addition, the **ac** component of the d_8 absorption was not observed by Sheka, probably because he used very thin samples. Several features associated with cluster states (*vide infra*) were also missing in Sheka's spectra.

The spectra obtained in the present work are shown in Fig. 2. The **ac** component of d_8 is easily identifiable. Unfortunately, due to the relative broadness of the **b** component of the h_8 absorption (and probably because of additional broadening due to the disorder), the two inner bands are barely separated at higher h_8 concentrations. Furthermore, fine structure, which is indeed very pronounced in the guest band involving mixed crystals of lower h_8 concentration, can be noted. These are absorption lines attributable to cluster states (dimers, trimers, etc.). Although these cluster states were expected within the theoretical framework presented in Paper I, the exact treatment has been hampered by both the lack of reliable dispersion relations and cumbersome mathematical manipulations.[12] In our numerical calculations, we have neglected the **k** dependence in the self-energy expression. This enables us to calculate the spectra using only the density-of-states functions. The same approximation also leads to the loss of fine structure in the calculated guest band. It is conceivable that a trial and error scheme involving an assumed dispersion relation to fit the spectra can be employed. In practice this might not be feasible. Here we choose to make some semiquantitative statements about the cluster states within a physically reasonable limit and draw some conclusions concerning the magnitude of the intermolecular interaction matrix elements that are responsible for the entire exciton band.

Cluster states in dilute mixed crystals have been investigated by Hanson[13] using crystals of larger thickness ($\sim$1 mm). Both the translationally inequivalent and translationally equivalent dimers were identified. Under Hanson's conditions (impurity concentration smaller than or equal to 1.4%), the host band was essentially unperturbed and isolated cluster states were the subject of study. The present problem is quite different in nature. Since appreciable amounts of impurities are introduced, interactions among these "islands" of clusters must be taken into account. It is only when the intermolecular interactions are really short range that some degree of simplification can be achieved. Under such conditions, the true cluster states can be correlated with isolated cluster states present in dilute systems. Fortunately, this seems to be the case for naphthalene. The spectrum of 10% h_8, except for relative intensity differences, resembles markedly that of the more dilute mixed crystals and the broadening is only slight. The following conclusions are drawn mainly from a study of h_8 cluster states. The corresponding d_8 states are obscure and less informative.

(1) It is noted that the 31 542 cm^{-1} peak assigned by Hanson *et al.*[1a] as the isolated impurity state of h_8 persists up to a concentration of almost 50% h_8. The same thing is probably true for the isolated impurity state of d_8 although it is obscured by the broad **b**-component of h_8 absorption and hence is only recognizable up to about 30% d_8. This is a strong indication that the intermolecular interactions are indeed short ranged. An isolated impurity state is essentially formed if the sites in the direct vicinity of the guest are occupied by host molecules. If the interactions were long ranged, such a state could hardly be described as "isolated."

(2) Two peaks to the lower energy side of the isolated impurity state are observed at 31 526 and 31 519 cm^{-1}. These peaks appear weakly at 10% h_8 (lost in the microphotometer tracing in Fig. 2) and become apparent at 30% h_8. Another weak line at 31 558 cm^{-1} was observed for 10% and 20% h_8. The lines at 31 526 and 31 519 cm^{-1} must be the **ac**-polarized absorption due to the translationally inequivalent dimer and trimer, respectively, judging from the intensity changes with respect to concentration. A simple calculation for isolated dimer and trimer places the corresponding energies at M_{12} and $\sqrt{2}M_{12}$ from the monomer line. Thus, if we take $M_{12}=16$ cm^{-1}, $\sqrt{2}M_{12}=22.5$ cm^{-1}, these two lines fall within the expected energy range. The 31 558-cm^{-1} line, which is 16 cm^{-1} to the blue of the monomer line, is assigned as the **b** component of the dimer absorption. Hanson[13] assigned the 31 519-cm^{-1} line as a lattice defect and the 31 558-cm^{-1} line as the naphthalene-βd_1 absorption. These do not necessarily contradict the present assignment since minute amounts of isotopic impurities and defects are unimportant for short path lengths of heavily doped mixed crystals as were studied in the present work.

(3) Broadening of the h_8 isolated impurity line was observed. The broadening is for the most part toward the red and is presumably caused by the translationally equivalent interactions. This is consistent with Hanson's[13] finding that translationally equivalent dimer lines appear to the red of the monomer line. No further information can be obtained concerning different translationally equivalent pairs due to the broadness of the line at this relatively high-impurity concentration.

From the above discussion, it is concluded in agreement with Hanson that the translationally inequivalent

interaction M_{12} between nearest neighbors is the largest intermolecular interaction in crystalline naphthalene. This interaction also contributes the major portion ($8M_{12}$) of the pure crystal Davydov splitting ($\sim$144 cm^{-1} out of a total of 158 cm^{-1}). It is worth noting that the density-of-states function calculated from these pairwise interactions has been shown by Hanson[13] to be in general agreement with the experimental results from the hot-band study. Our calculations are thus self-consistent.

Examining carefully the published spectra of Sheka,[6] it is noted that the B_1^1 band (the **b**-polarized Davydov component of h_8) at low h_8 concentrations is probably the largely **b**-polarized isolated impurity state near 31 542 cm^{-1}. Since Sheka assumed a concentration-dependent ϵ_{h_8}, this assignment appeared to be self-consistent. However, Sheka's own spectra also show that this band actually has a small amount of **ac** polarization. Our spectra show that the 31 542-cm^{-1} band persists up to 50% h_8. This is probably why the B_1^1 band of Sheka appears to be nearly concentration independent over a wide range of low h_8 concentrations. This band then undergoes an abrupt change when C_{h_8} is near unity. This misinterpretation of the isolated impurity absorption plus the fact that Sheka's spectra were taken at 20°K and hence are structureless might have led Sheka to overlook the possibility of cluster states. Consequently, he and probably also Broude and Rashba[7] inferred that heavily doped mixed crystals behave like pure crystals with Davydov splittings associated with each component throughout the entire concentration range. From the present study, it would appear to us that it is only legitimate to speak of "quasi-Davydov splitting" where the concentration of the component in question reaches 50% or more. At low concentrations the terms Davydov components and Davydov splittings are only meaningful in an average sense. This is exactly why our calculations that treat the cluster states in an average manner do show a broad **ac** component and a broad **b** component reminiscent of the Davydov splitting in pure crystals.

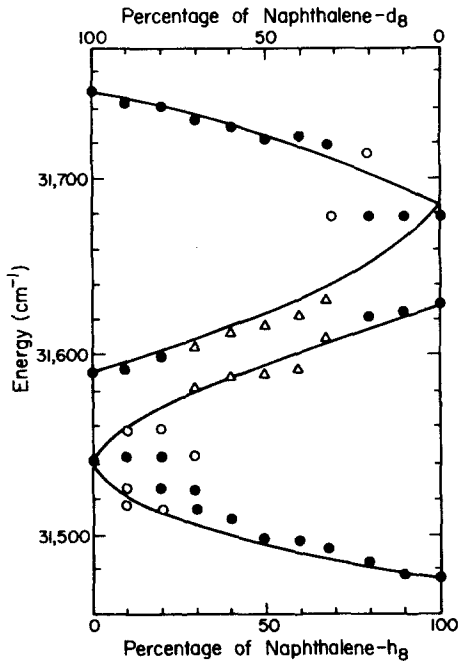

FIG. 3. The positions of the absorption peaks vs concentration for naphthalene-h_8 and -d_8 mixed crystals as observed in this work. The solid circles represent strong lines easily identified from Fig. 2. The open circles represent absorptions that are very weak and often not evident in Fig. 2. The triangles represent peaks whose positions are only estimated from Fig. 2 due to large overlapping. The solid curves are the calculated results.

In Fig. 3, we compare our experimental results with calculations presented in I, using the experimental density-of-states function of Colson *et al.*[4] It is noted that the agreement is fairly good except for the guest band at low concentrations. Calculations based on the density-of-states function of the octopole model because of its large asymmetry do not coincide with the observed spectra. On the other hand, using the correct values of ϵ_{h_8} and ϵ_{d_8}, the formula of Broude and Rashba will yield incorrect isolated impurity levels. Furthermore, this formula predicts that the **ac**-polarized band of d_8 will be concave down and the **b**-polarized band of h_8 will be concave up (see the inner bands in Fig. 1). The effect of the guest on the host band is thus much overestimated. The experimental density-of-states function leads to larger discrepancies when an impurity is placed above the host band. This is reflected in a slightly larger deviation for the d_8 bands.

The comparison of intensity distributions and line shapes between theory and experiment cannot be made easily. Both the Green's function method and the model of Broude and Rashba predict the enhancement of outer bands and the weakening of the inner band. Sheka found this to be true but offered no quantitative discussion. In the present investigation, thicker samples are used and much of the absorption appears to be almost complete. Intensity measurements are therefore not very reliable. The overlapping of inner bands also complicates the situation. As to the line shapes, it can be noted that the **ac**-polarized h_8 absorption does behave as predicted. The **b**-polarized absorptions are intrinsically broad, perhaps because of phonon participation, and appear to be somewhat dependent upon crystal preparations. Further broadening due to disorder cannot be assessed from the spectra.

From the above discussion, the theory presented in I provides a good description of the basic physics concerning the energy states of heavily doped mixed crystals. Agreement between the theoretical results was found to be good for the host band. In the guest band, fine structure due to cluster states was not accounted for by the approximate calculations. These

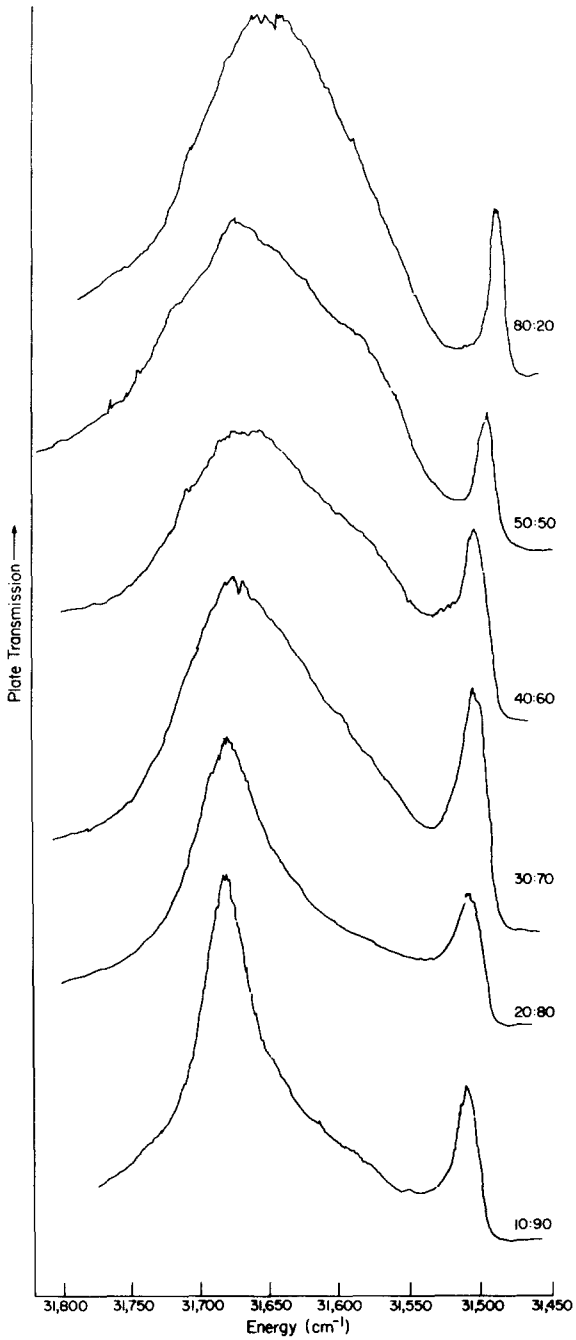

FIG. 4. The absorption spectra of naphthalene-h_8 and -αd_4 mixed crystals. The ratios correspond to naphthalene-h_8:naphthalene-αd_4 given to the closest 10%($\pm$2%).

features are discussed here semiquantitatively. Future improvement on the theory will have to consider contributions from exciton–phonon interactions and higher-order self-energies.

2. *Naphthalene-h_8 and Naphthalene-αd_4*

With an energy gap of 51 cm^{-1}, this system represents a case in between the very strong perturbation in one limit and the very weak perturbation in the other. The perturbation is neither strong enough to separate the guest band from the host band nor weak enough to retain the **k** symmetry. Two absorption bands were predicted by the numerical calculations in I. These two bands are broadened by the **k** mixing and their energies are predicted to vary nonlinearly with concentration.

In the limit of infinitely dilute naphthalene-h_8 in a naphthalene-αd_4 host, a bound naphthalene-h_8 level 1 cm^{-1} below the αd_4 band edge is predicted by the theory[1] (using the experimental density-of-states function by Colson *et al.*[4]). In addition, for dilute naphthalene-αd_4 in a naphthalene-h_8 host the theory of Koster and Slater[1] yields a virtual state of αd_4 10 cm^{-1} below the **b** component of h_8. On the experimental side, the h_8 isolated impurity state was observed by Broude *et al.*[14] at 31 519$\pm$2 cm^{-1} (7$\pm$4 cm^{-1} below the αd_4 band edge). No evidence has yet been found for the virtual state of dilute αd_4 in the h_8 mixed crystal.

For the heavily doped (10%–90%) mixed crystal, theory[2] predicts that at 10% h_8 the **b** component of αd_4 remains sharp whereas the **ac** component is somewhat broadened due to the interaction between the αd_4 **k**=**0** state and the h_8 impurity state. The perturbation comes from below the band. As the h_8 concentration increases, the **ac** component becomes sharper and the **b** component becomes broader. At 10% αd_4, the virtual state of αd_4 appears as a background shoulder below the **b**-component absorption of h_8. The perturbation now affects mostly the states near the top edge of the h_8 band.

The spectra of h_8 plus αd_4 are shown in Fig. 4. The main features are consistent with the theoretical predictions laid out in the preceding paragraph. Broude *et al.*[4] reported that at low concentrations ($\ll$10%) the h_8 impurity absorption is almost as intense as the **ac** component of αd_4 due to the strong intensity borrowing from the host (known as Rashba's effect[15]). As the concentration of h_8 increases, the intensity of the h_8 band should increase while that of αd_4 diminishes. This explains why at 10% h_8 a single band showing broadening toward the blue is observed. The virtual states in dilute mixed crystals have never been observed experimentally. Granted that the experimental density-of-states is essentially correct, the virtual states are only expected when impurity states are above the band. The broad **b** component makes such observations extremely difficult. In the 20% αd_4 spectrum, broadening of the **b**-component absorption of h_8 can be noted. This broadening might loosely be designated as due to the virtual states of αd_4. If the αd_4 concentration were reduced, theory predicts that a single level separated from the **b** component of h_8 exists; however, since this **b** component is so broad, the αd_4 absorption will certainly be obscured. Similar difficulties also prohibit the observation of the βd_4 virtual state.[6] It would

appear that virtual states are only evident in the spectra of heavily doped mixed crystals, and in naphthalene isotopic mixed crystals only then as a broadening rather than a truly resolved transition.

The nonlinearity is apparent in Fig. 5 where the positions of the **ac** and **b** components are plotted against concentration. The slightly large discrepancies involving the **b** component absorption reflect largely the uncertainties in measuring broad lines. Although the formula of Broude and Rashba[7] predicts a similar concentration dependence for the outer bands, it fails to account for the broadening. The four-level scheme of Broude and Rashba also gives two inner bands shown by dotted lines in Fig. 5. According to their analysis, the intensity of an absorption line is proportional to the quantity $F(E_{\lambda\rho})$ given by

$$F(E_{\lambda\rho})=\frac{[(C_1/\epsilon_1-E_{\lambda\rho})+(C_2/\epsilon_2-E_{\lambda\rho})]}{[C_1/(\epsilon_1-E_{\lambda\rho})^2]+[C_2/(\epsilon_2-E_{\lambda\rho})^2]}, \quad (3)$$

where $E_{\lambda\rho}$ is the λth root of the energy secular equation and corresponds to the excitation of the λth component. The factor-group classification is designated by ρ, the concentrations by C, and the ideal mixed crystal levels by ϵ. The intensity distributions calculated from Eq. (3) show that the outer bands carry as much as 90% or more of the oscillator strength with the remaining 10% or less being carried by the inner bands. The prediction concerning the existence of these inner bands not only disagrees with the experiments but also presents some conceptual difficulties that must be regarded as inherent in the four-level scheme (*vide infra*).

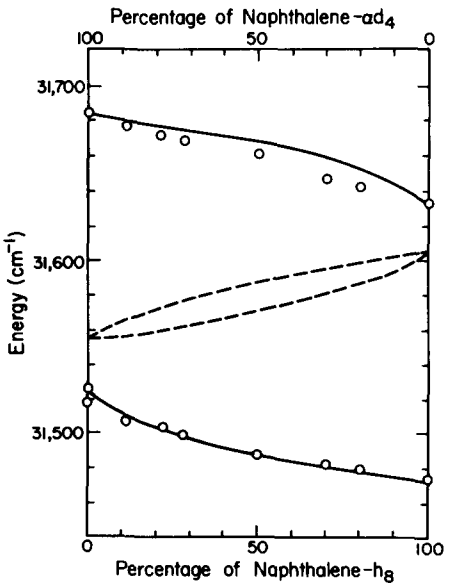

FIG. 5. The positions of the Davydov components vs concentration for naphthalene-h_8 and -αd_4 mixed crystals. The solid curves are calculated results in I[2]. The dotted lines indicate extra bands obtained from the formula of Broude and Rashba. See text.

In our model calculation, the inner bands show both broadening and weakening at large perturbation strength. In going from a strong to a weak perturbation, the inner bands disappear smoothly while the outer bands show a long tailing towards the inner band region. As pointed out in I, this difference in the theoretical descriptions of the energy states is basically a result of different starting points. Our formulation allows random distribution of impurities while only one configuration is considered in the model of Broude and Rashba.

Finally, according to the model of Broude and Rashba, the two long-wavelength bands are portrayed as the **ac** and **b** components of h_8 absorptions and the other two short-wavelength bands as the corresponding αd_4 absorptions. (In Sheka's notation they are A_1^1, B_1^1, A_1^2, and B_1^2, respectively, in the order of increasing energy.) The energy difference between A_1^1 and B_1^1 (between A_1^2 and B_1^2) is regarded as the "Davydov splitting" of h_8 (of αd_4). It is built into the theory of Broude and Rashba that the sum of the two Davydov splittings is always equal to the Davydov splitting in the pure crystal. (This can be seen from Fig. 5.) This picture is quite misleading in many ways. For example, the A_1^1 band, which is presumably designated as such to mean the **ac**-polarized excitation of h_8, actually involves the excitation of both h_8 and αd_4, as does the B_1^2 band. The B_1^1 band, which is designated to mean the **b**-polarized absorption due to h_8, actually does not converge to the **b** component of pure h_8 absorption. The same thing can be said about the A_1^2 band. Our interpretation of the energy system represented in earlier sections is void of such contradictions. Even though the magnitude of the splitting in the mixed crystal is different from that in the pure crystal, the two bands can certainly be regarded as the Davydov splitting in the mixed crystal since their direct parentage can be traced to the Davydov splitting in the pure crystal.

3. *Naphthalene-h_8 and Naphthalene-βd_1*

In our formulation presented in I, the average Green's function is expressed as an infinite perturbation expansion involving different powers of (Δ/T), where Δ is the perturbation strength and T is the bandwidth. For the naphthalene-h_8–naphthalene-βd_1 system, the energy gap is 21 cm^{-1} (compared with a total exciton bandwidth of $\sim$160 cm^{-1}). $\sum(\mathbf{k}, E)$ is very small and the expansion is expected to converge rapidly. In this weak perturbation limit,

$$\langle G(\mathbf{k}, E)\rangle \cong 1/[E-C_A\epsilon_A-C_B\epsilon_B-\epsilon(\mathbf{k})];$$

hence the **k** mixing is negligible and the whole band is shifted from the band center of ϵ_A to $C_A\epsilon_A+C_B\epsilon_B$. The position of each $\mathbf{k}=\mathbf{0}$ level is a linear function of concentration and practically no broadening is ex-

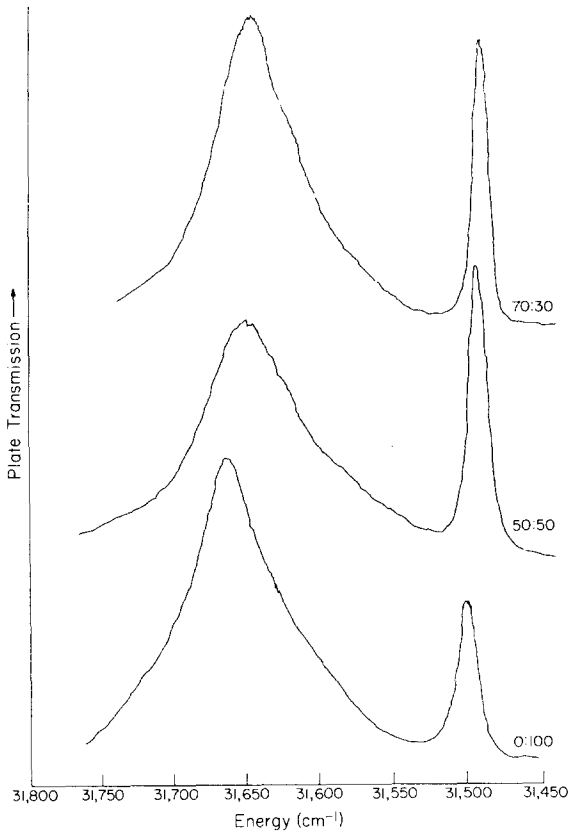

FIG. 6. The absorption spectra of naphthalene-h_8 and -βd_1 mixed crystals. The ratio corresponds to naphthalene-h_8:naphthalene-βd_1 given to the closest 10%(±2%).

pected. In the limit of infinite dilution, no solution to the equation of Koster and Slater[1] for isolated impurity can be obtained.

The observed spectra are shown in Fig. 6. They indeed resemble the spectra of pure crystals in that no appreciable broadening is present. Similar plots of line positions vs concentration are shown in Fig. 7 and yield a straight line. This observation is also in agreement with the theory. It should be noted that the model of Broude and Rashba again predicts two "inner bands" plotted as a dotted line in Fig. 7. Although the intensities of the inner bands calculated from Eq. (3) are only about 1% of the total intensity, and would therefore not be expected to be observed, inherent difficulties with this model are present as before.

B. Band-to-Band Transitions

1. General Discussion

The usefulness of studying band-to-band transitions in molecular crystals has long been recognized. Rashba[16] first proposed the method in connection with the study of exciton density of states. Its recent application to crystalline benzene and naphthalene was carried out by Colson *et al.*[4] Due to the familiar $\Delta\mathbf{k}=\mathbf{0}$ selection rule, the standard spectroscopic data involve only the optical transitions from the vibrationless ground state to some specific points (i.e., the points where $\mathbf{k}=\mathbf{0}$) in the exciton Brillouin zone. In band-to-band transitions, however, the initial states consist of all the $\mathbf{k}$ states in the vibrational (or electronic) exciton band and hence optical transitions to all the $\mathbf{k}$ states of the electronic (or vibrational) exciton band are accessible to spectroscopic investigation. Further simplification can be achieved if the vibrational exciton bandwidth is much smaller than the electronic exciton bandwidth. In this case, band-to-band transitions will directly yield information concerning the density of states of the electronic exciton band.

In the formulation presented in I[2], calculations were done only for the upper states. Similar calculations can also be done for the vibrational exciton band. This type of calculation would involve somewhat different vibrational excitations of the two different components. However, it is now known that vibrational exciton bandwidths in molecular crystals are likely to be of the order of a few wavenumbers. If the perturbation is strong, the weak intermolecular interactions are too small to induce coupling between the two vibrational bands. On the other hand, if the perturbation is weak, the resulting bandwidth would be very small compared to the electronic exciton bandwidth. In either case, detailed calculations concerning the vibrational band structure would be unnecessary in interpreting the band-to-band spectra. Therefore, in the following analysis the exciton behavior of the ground state vibra-

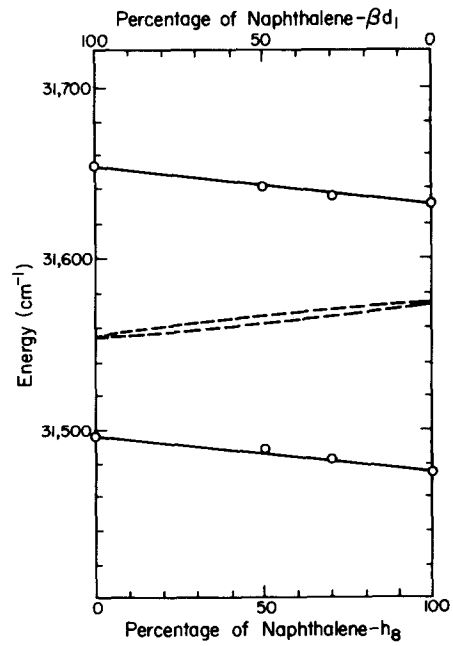

FIG. 7. The positions of the Davydov components vs concentration for naphthalene-h_8 and -βd_1 mixed crystals. The solid curves are calculated results in I[2]. The dotted lines indicate extra bands obtained from the formula of Broude and Rashba. See text.

tional band will be neglected. Vibrational levels will simply be treated as a degenerate set of levels rather than as a band.

When the coupling between vibrational levels is neglected, it is logical to use the localized representation,[17]

$$\chi(\mathbf{R}_i)=\phi_{\text{vib}}^*(\mathbf{R}_i)\prod_{j\neq i}\phi_{\text{vib}}(\mathbf{R}_j), \tag{4}$$

where $\phi_{\text{vib}}^*(\mathbf{R}_i)$ denotes vibrational excitation at site $\mathbf{R}_i$, and $\phi_{\text{vib}}(\mathbf{R}_j)$ corresponds to the vibrationless wavefunction at site $\mathbf{R}_j$. It is to be understood that the electronic eigenfunction corresponding to the ground electronic state is included as a factor in $\chi(\mathbf{R}_i)$. Using this representation, all the $\chi_A(\mathbf{R}_n)$'s corresponding to the excitation of A molecules will be degenerate and independent of site index n, as are the $\chi_B(\mathbf{R}_m)$'s. Thus we have two sets of degenerate levels, one with energy ϵ_A^{vib} and the other ϵ_B^{vib}, the degree of degeneracy being equal to the number of molecules of the component in question, namely, N_A or N_B.

Now consider a particular distribution of hosts and guests. In terms of a localized basis set the electronic wavefunction of a particular level k with energy E_k can be written as

$$\Phi^k=\sum_i \mathfrak{a}_i^k\Psi(\mathbf{R}_i), \tag{5}$$

where $\Psi(\mathbf{R}_i)$, similar to $\chi(\mathbf{R}_i)$ in Eq. (4), denotes electronic but no vibrational excitation at site i, molecules at all other sites being in their ground states, and the summation is to be carried out over all sites in the crystal. Linear combination of one-site excitation functions is necessary because of the larger mobility of the electronic excitons. The transition moment between the k level and, say, one of the vibrational levels having energy ϵ_A^{vib} is

$$\sum_i \mathfrak{a}_i^k\langle\Psi(\mathbf{R}_i)\,|\,\mathbf{M}\,|\,\chi_A(\mathbf{R}_n)\rangle=\mathfrak{a}_n^k\mathbf{M}_A, \tag{6}$$

where $\mathbf{M}_A$ is the transition moment of the same transition in the free molecule A. Since all the vibrational excitations of A in different sites are degenerate, the total intensity of the transition $E_k\leftrightarrow\epsilon_A^{\text{vib}}$ is simply

$$|\,\mathbf{M}_A\,|^2\sum_n|\,\mathfrak{a}_n^k\,|^2, \tag{7}$$

where $\sum_n$ denotes summation over all A sites. Similarly, the transition $E_k\leftrightarrow\epsilon_B^{\text{vib}}$ will carry the intensity

$$|\,\mathbf{M}_B\,|^2\sum_m|\,\mathfrak{a}_m^k\,|^2, \tag{8}$$

with $\sum_m$ denoting summation over B sites, and

$$\sum_n|\,\mathfrak{a}_n^k\,|^2+\sum_m|\,\mathfrak{a}_m^k\,|^2=1,$$

because the wavefunction is normalized.

Normally, if we consider closely related vibrational levels of A and B, $\mathbf{M}_A$ and $\mathbf{M}_B$ are essentially the same. Under this condition a comparison of intensities of the transition $E_k\leftrightarrow\epsilon_A^{\text{vib}}$ and of $E_k\leftrightarrow\epsilon_B^{\text{vib}}$ will reveal the true nature of the excitation involved in level k, i.e., whether it is pure A excitation, pure B excitation, or a mixture of the two. This is the technique of Broude *et al.*[18] for determining the excitation amplitude at impurity centers in dilute mixed crystals of isotopic naphthalenes. However, the assumption that $\mathbf{M}_A\cong\mathbf{M}_B$ was neither clearly stated nor carefully examined.

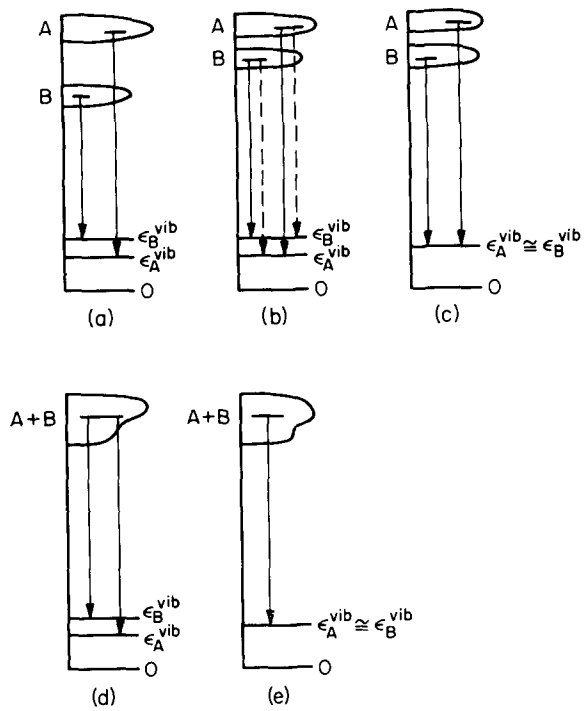

FIG. 8. Schematic diagrams of band-to-band transitions in mixed crystals. The electronic exciton bands are shown with finite bandwidth while the vibrational exciton bands are assumed to be of delta-function type. Possible transitions are indicated by arrows. ϵ_A^{vib} and ϵ_B^{vib} are vibrational quanta of the A molecule and the B molecule, respectively.

Notice that, compared with the case of a pure crystal, the approximation used here is more restricted than the "restricted Frenkel limit" of Colson *et al.*[4] Delocalized sets were used by Colson *et al.* although the finite vibrational exciton bandwidth was neglected. In the localized limit used here, the band-to-band transition in a pure crystal can still be interpreted in terms of the density-of-states function. Instead of using the $\Delta\mathbf{k}=\mathbf{0}$ selection rule for the $\mathbf{k}\neq\mathbf{0}$ state to prove that intensity is conserved, the normalization condition here guarantees the same result.

When configuration averaging of random lattice is carried out, k states may change their characteristics. In this case the band-to-band transition is rather difficult to discuss. It is only under two conditions that the band-to-band spectra can be interpreted simply as the density-of-states function:

(1) $\sum_n|\,\mathfrak{a}_n^k\,|^2\cong1$, $\sum_m|\,\mathfrak{a}_m^k\,|^2\cong0$, or vice versa;

(2) $\epsilon_A^{\text{vib}}\cong\epsilon_B^{\text{vib}}$.

TABLE I. Fluorescence spectra of naphthalene-h_8 and -d_8 mixed crystals (in cm^{-1}).

90:10[a]			70:30[a]		30:70[a]		10:90[a]	
$\tilde{\nu}$	$\tilde{\nu}-\nu_{0-0}$[b]	Assignment	ν	$\Delta\nu$[c]	ν	$\Delta\nu$[c]	ν	$\Delta\nu$[c]
30 967	510	$\nu_{17}(b_{3g})$, $\nu_1(a_g)$[d]	30 975	8	30 991	24	31 014	47
							31 006	39
30 713	764	$\nu_2(a_g)$	30 720	7	30 735	22	...	...
30 540	937	$\nu_{18}(b_{3g})$	30 545	5	30 560	20	30 587	47
							30 579	39
30 454	1023	509+514	30 461	7	30 478	24	30 500	46
							30 494	40
30 201	1276	510+764	30 208	7	30 222	21	...	...
30 094	1383	$\nu_5(a_g)$	30 100	6	30 115	21	30 141	47
							30 133	39
30 032	1445	510+937	30 038	6	30 052	20	...	...
30 018	1459	$\nu_6(a_g)$	30 025	7	30 040	22	...	...
29 943	1534	2×764	29 948	5	29 966	23	...	...
29 849	1628	$\nu_{22}(b_{3g})$	29 855	6	29 871	22	...	...
29 584	1893	510+1383	29 590	6	29 605	21	29 631	47
							29 624	40
29 165	2312	Impurity?	...	...	...	...	...	...
29 155	2322	937+1383	29 160	5	29 177	22	...	...

[a] The ratio given refers to naphthalene-h_8: naphthalene-d_8.

[b] 0–0 is missing due to reabsorption. The value used here, 31 477 cm^{-1}, is measured from the absorption.

[c] $\Delta\nu$ refers to $\nu-\tilde{\nu}$, where $\tilde{\nu}$ is the value given in the first column.

[d] ν_1 and ν_{17} are nearly degenerate. Broude *et al.*[22] reported them to be 514 and 509 cm^{-1} in the crystalline state. They are unresolved here.

In Toyozawa's language,[19] case (1) would be a strong persistent type↔strong persistent type transition, while case (2) would be a persistent or amalgamated type (electronic band)↔amalgamated type (vibrational band) transition. In Fig. 8 we illustrate different situations diagrammatically. It can be seen that only in cases (a), (c), and (e) can the band-to-band transitions be directly related to the density-of-states function.

Finally, it should be pointed out that the excitation amplitude $\mathfrak{A}_i^k$ can *not* be calculated from the average Green's function obtained in I. It is necessary to calculate the excitation amplitude for each individual Green's function by solving the equation

$$\mathbf{G}^{-1}\mathfrak{A}=0$$

and then average over all impurity distributions, rather than solving a similar equation involving the average Green's function. In order to determine the nature of the excitation we will have to resort to experimental observations.

2. *Naphthalene-h_8 and Naphthalene-d_8*

The fluorescence spectra of napthalene-h_8 and -d_8 mixed crystals were taken at 4°K to determine (1) whether the low-energy absorption edge is actually the edge of the density-of-states function as predicted by the theoretical calculations, (2) whether it is justifiable to neglect the exciton behavior of the vibrational exciton band in the ground electronic state, and (3) whether any cooperative electronic excitation[18] involving both the host and the guest actually occurs in this particular system.

The positions of the sharp emission lines and their assignments are given in Table I. The 0–0 transitions are very weak in each case due to strong reabsorption; however, they can be located by adding a constant quantum of 510 cm^{-1} corresponding to ν_{17} (or ν_1, *vide infra*) to the first strong vibronic bands. The positions of the band edges in the upper state can thus be determined. From a comparison of Table I and Figs. 2 and 3, it can be seen that the band edges coincide with the absorption edges in agreement with our theoretical predictions. Furthermore, constancy of the vibrational intervals is observed. As shown in the $\Delta\nu$ columns of Table I, the spectra have similar vibronic structure built on varying origins. If the interactions between the vibrational levels were strong, resonance interactions would cause the spreading of the vibrational states and quasiresonance interactions would induce coupling between the vibrational levels of host and guest. None of these effects is observed, indicating that vibrational excitations are essentially localized. The widths of the vibronic bands, which are roughly 10 cm^{-1}, are about the same as those of the pure crystal fluorescence. The widths are believed to be due either to thermal population of the upper states, or intrinsic linewidth, or both. It follows from a comparison between the linewidths of mixed crystals and those of pure crystals that the vibrational interactions cannot be larger than a few wavenumbers. In fact, the only factor-group splitting observed in the pure crystal Raman spectra measures only 0.7 cm^{-1}.[20]

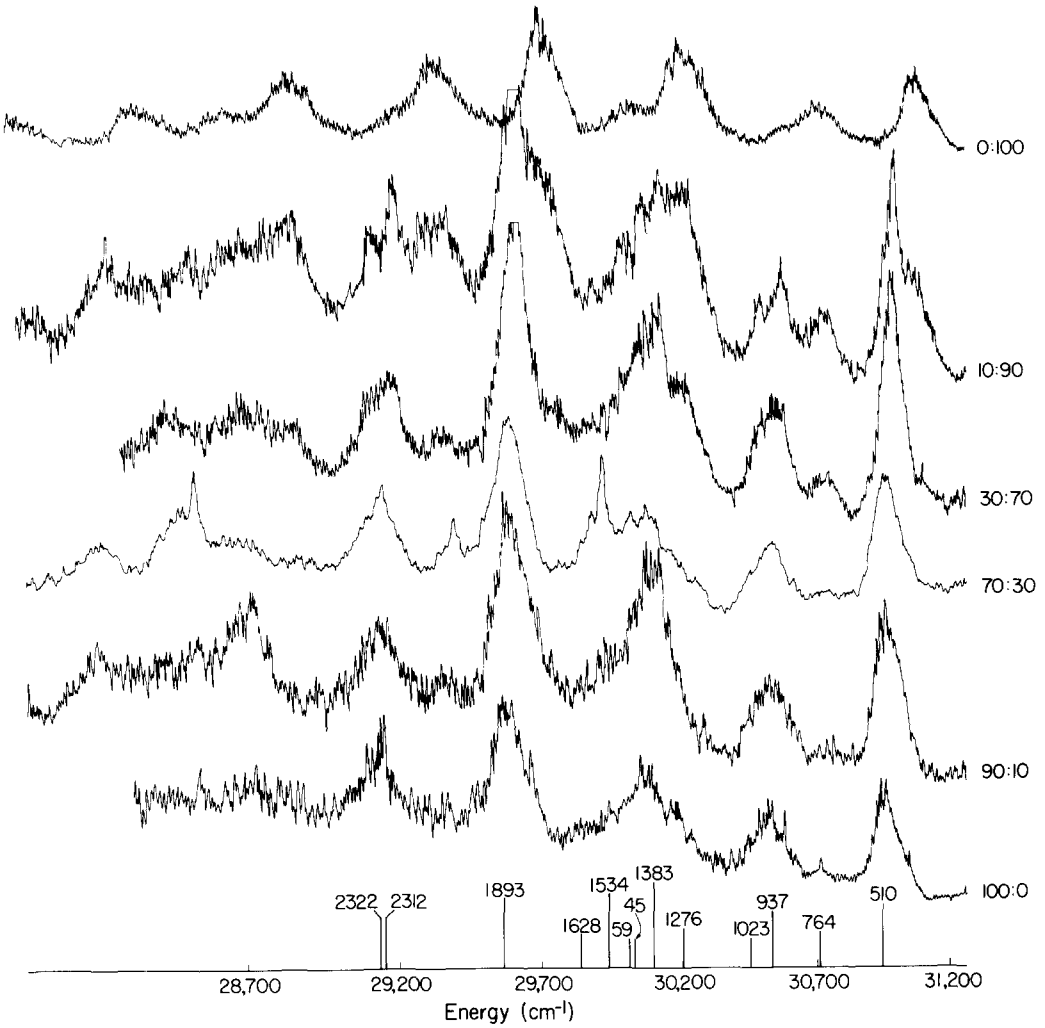

FIG. 9. Fluorescence spectra of naphthalene-h_8 and -d_8 mixed crystals at 77°K. The ratios correspond to naphthalene-h_8: naphthalene-d_8 given to the closest 10% (±2%). Vibrational analysis is given at the bottom of the figure.

The spectrum of 10% h_8 in d_8 has two origins: one coincides with the dimer state discussed in Sec. III.A.1, and the other coincides with the trimer state (within the experimental uncertainty caused by the width of the vibronic bands). This fact not only supports the idea of a localized vibrational excitation but also indicates that the density-of-states function is probably not continuous at this concentration. Due to the breakdown of the $\Delta\mathbf{k}=\mathbf{0}$ selection rule in mixed crystals, any state, whether optically active or not in ordinary absorption, can be observed in a band-to-band transition.[21] The fact that two relatively sharp lines are observed instead of a broad band must mean that there are few or no states between the dimer and the trimer states.

The analysis of the vibronic structure given in Table I is essentially the same as that of Broude *et al.*[22] and Pröpstl and Wolf[23] for the pure crystalline h_8 fluorescence. It also correlates well with McClure's[24] fluorescence results of naphthalene in durene and the gas-phase hot-band data of Craig *et al.*[25] The 510 cm^{-1} vibration has been shown by Broude *et al.* to be an unresolved band involving both a b_{3g} vibration (ν_{17}) and an a_{1g} vibration (ν_1). The 1023-cm^{-1} band, which is nearly degenerate with $\nu_3(a_{1g})$, is assigned here as $\nu_{17}+\nu_1(b_{3g})$ in accordance with Craig's polarization results. The 937-cm^{-1} band was also assigned by Broude *et al.* to be an unresolved band of 935 cm^{-1} (b_{3g}) and 940 cm^{-1} (a_{1g}). It is assigned here as $b_{3g}(\nu_{18})$ alone since no a_{1g} vibration of 940 cm^{-1} was observed in the pure crystal Raman spectrum.[20] The 1459 cm^{-1} line was reported by Broude *et al.* but left unassigned. It is tentatively assigned as ν_6 corresponding to the Raman value of 1464 cm^{-1}.[20]

In the search for d_8 vibrations, we concentrated on regions near the four bands at 510, 764, 937, and 1383 cm^{-1}, corresponding to the h_8 vibrations ν_{17}, ν_2, ν_{18}, and ν_5, respectively. It was reported by Broude *et al.*[18] that at low concentrations of h_8 cooperative excitation

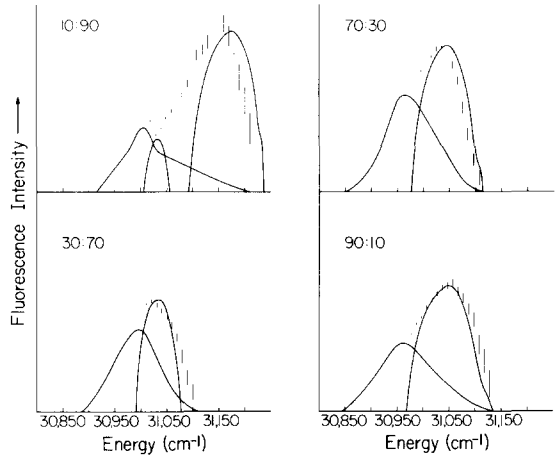

FIG. 10. The density-of-states functions of naphthalene-h_8 and -d_8 mixed crystals calculated from the fluorescence band shapes. The vertical bars are error bars. The fluorescence intensity to the red of the band edge is attributable to phonons and not corrected with Boltzmann factors. The solid curves approximately enclosed by the error bars are theoretical density-of-states functions from Paper I. For a fuller description of the 10% naphthalene-h_8 spectrum, see text. The ratios correspond to naphthalene-h_8: naphthalene-d_8 given to the closest 10% (±2%).

does take place. This conclusion was based on the finding that a d_8 vibration of 496 cm^{-1} occurs. From the observed intensity, the excitation amplitude at the mpurity center was set to be 0.9. As we pointed out in the previous section, a cooperative excitation can only be positively identified if a large part of the host spectrum is observed in a supposed guest emission. The naphthalene-d_8 emission has been studied by McClure[26] in a durene host. The ground state fundamentals were also determined from hot-band absorption by Craig and Hollas.[27] These two sources are in general agreement, although McClure's spectra seemed to be more complicated possibly due to the presence of isotopic impurities. The corresponding vibrations of ν_{17}, ν_2, ν_{18}, and ν_5 of d_8 are found to be 492, 694, 880, and 1380 cm^{-1}. Of all the four vibrations only the first one was identified by Broude *et al.*[18] and none is apparent in our spectra. It is thus concluded that although some degree of cooperative excitation might be operating at low naphthalene-h_8 concentration, for heavily doped mixed crystals the low energy band edges are mainly comprised of naphthalene-h_8 states. Stated equivalently, the excitation is mainly localized on naphthalene-h_8 centers.

To investigate the entire h_8 band, we resorted to the study of band-to-band transitions at elevated temperatures. Fluorescence spectra at 77°K are shown in Fig. 9. Two features can be noted: firstly, the peaks show a gradual shift to higher energy as the concentration of naphthalene-h_8 is reduced, and secondly, the bandwidth decreases in the same direction, especially the 510 and 1893 cm^{-1} bands, which are relatively isolated. The corresponding transitions at 4°K are also given at the bottom of the figure for comparison. The large amount of overlapping causes the identification of an individual band to be more difficult; however, in each case the positions of the strong peaks do correlate well with the sharp lines at 4°K.

It is apparent that only the well separated bands at 510 and 1893 cm^{-1} can be utilized in evaluating the density of states in mixed crystals. Since these two peaks are broad at 77°K and the difference in vibrational energies is small (~10 cm^{-1}), the question of whether cooperative excitation exists cannot be answered with certainty. However, the density-of-states functions can still be calculated from the fluorescence band shape. This fact is concluded from the following considerations:

(1) Cooperative excitation as observed in fluorescence is equivalent to splitting the density-of-states function into two parts and shifting one part from the other by the amount equal to the difference in energies of vibrational quanta (~10 cm^{-1} in this case). Since the h_8 bandwidth is large compared to this shift, the effect of cooperative excitation on the fluorescence band shape is insignificant. Considering the much larger experimental uncertainties in measuring the band shape and intensity, this effect can be safely neglected. This would put the naphthalene-h_8 and -d_8 systems into the category of case (c) in Fig. 8.

(2) On the other hand, the 4°K spectra that are well resolved give no indication of cooperative excitation. The 77°K spectra, although less certain, do not seem to involve large cooperative excitation either. From this point of view, this system would belong to case (a) in Fig. 8. In both cases, the density-of-states function is directly related to the fluorescence band shape.

The 510 cm^{-1} band has been singled out and carefully scanned to obtain the best band shape. The method of Colson *et al.*[4] for determining the pure crystal density-of-states function was used. The fluorescence data at 4°K serve to locate the band edge, and the intensity of emission to the blue of the band edge is corrected with proper Boltzmann factors at 77°K. The results are shown in Fig. 10. Also included in the figures are the density-of-states functions theoretically calculated in I.[2] The h_8 and d_8 contributions were properly proportioned and separated by 10 cm^{-1} to account for the difference in vibrational excitation energies. These density-of-states functions were drawn such that the heights roughly match the experimentally determined height. In the 10% h_8 fluorescence spectrum, the shoulder to the blue of the band edge was taken as the host emission. Similar to the pure crystal case, what appear to be large phonon contributions to the red of the band edge can be noted. A band-to-band absorption (hot band) would probably be clear of such complica-

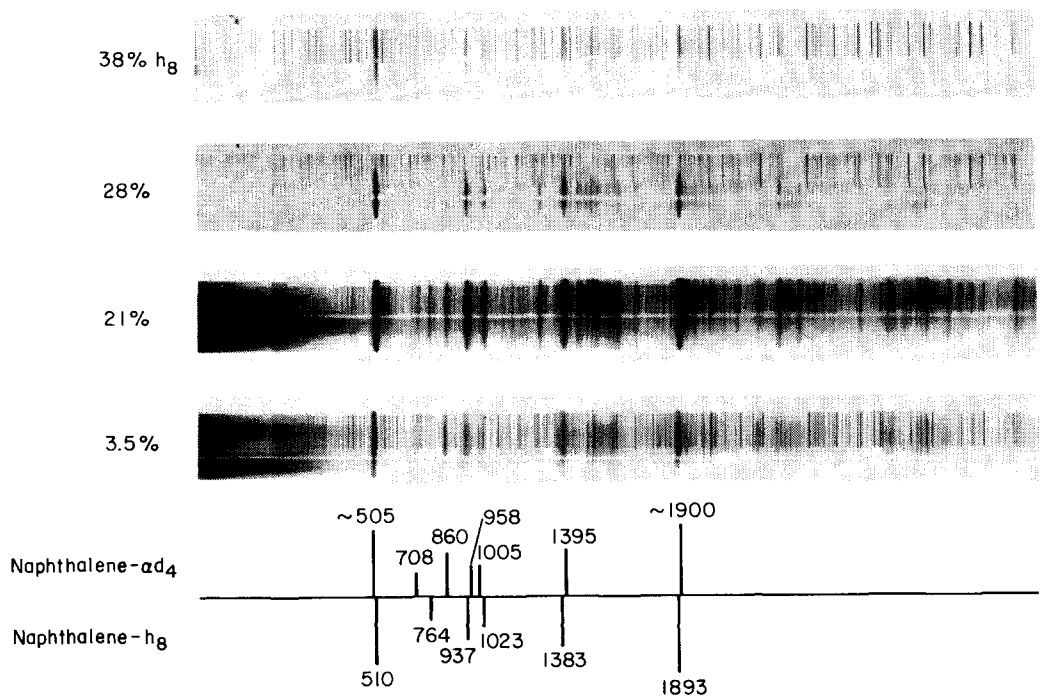

FIG. 11. The fluorescence spectrum of naphthalene-h_8 and -αd_4 at 4°K. The vibrational analysis is given at the bottom of the figure.

tions; however, since the features are so similar to those that occur in the pure crystal emission, which has been thoroughly investigated in the past, no further attempt was made to show that they are indeed due to phonons.

The agreement between theory and experiment is generally good. The emission intensity in between the host and guest density-of-states functions in the 10% sample could be due to the phonon associated with the host emission, or due to the cooperative excitations discussed above, or both. The density-of-states function in the guest band is probably not continuous for the 10% sample. The continuous curve observed experimentally must be due to the effect of phonon broadening.

3. *Naphthalene-h_8 and Naphthalene-αd_4*

As shown in Fig. 4, the absorption spectrum of the napthalene-h_8–naphthalene-αd_4 shows only one **ac** component. This observation is consistent with the theoretical model. The **ac**-polarized absorption can only be interpreted as a cooperative excitation of both h_8 and αd_4. This interpretation is substantiated by the vibrational analysis of the emission spectrum at 4°K shown in Fig. 11. For comparison, the bands that are attributable to h_8 are also given. Additional bands assigned as αd_4 vibrations are found at 708, 860, 958, 1005, and 1395 cm^{-1}, respectively. The positions of these bands vary with concentration, whereas their relative positions with respect to the h_8 bands remain unchanged. Furthermore, their intensity diminishes as the concentration of naphthalene-h_8 increases. This evidence shows that they are indeed originating from the same upper state and hence cannot be assigned as impurity emission. The prominent lines at 510 and 1893 cm^{-1} are much broader ($\sim$20 cm^{-1}) than the rest of the bands. They must be unresolved h_8 plus αd_4 bands. As expected, at higher h_8 concentrations these two bands become sharper while the other αd_4 bands reduced in intensity. All the facts indicate a gradual decrease in the degree of cooperative excitation with decreasing concentration of αd_4.

The emission spectrum of naphthalene-αd_4 is not available in the literature; however, normal mode calculations have been carried out by Freeman and Ross[28] and the Raman spectrum in the liquid state has been observed by Mitra and Bernstein,[29] both aiding in the vibrational assignment. In all probability the 708 and 1005-cm^{-1} bands are αd_4 analogues of the 764 and 1023-cm^{-1} bands in the h_8 emission. ν_5 for αd_4 has been calculated to be 1340 cm^{-1}; however, the next-higher-frequency a_{1g} vibration, namely, the 1395-cm^{-1} vibration, seems to be the counterpart of the 1383-cm^{-1} band in h_8. Frequencies at both 1355 and 1397 cm^{-1} were identified in the Raman spectrum of αd_4. The 860 and 958-cm^{-1} bands were assigned by Mitra and Bernstein[29] as a_{1g} and b_{3g}, respectively. Our results would classify both bands as b_{3g}, since they seem to play roughly the same role as the ν_{18} 937-cm^{-1} band in h_8 with 860 cm^{-1} carrying most of the fluorescence intensity. However, Mitra and Bernstein assign still

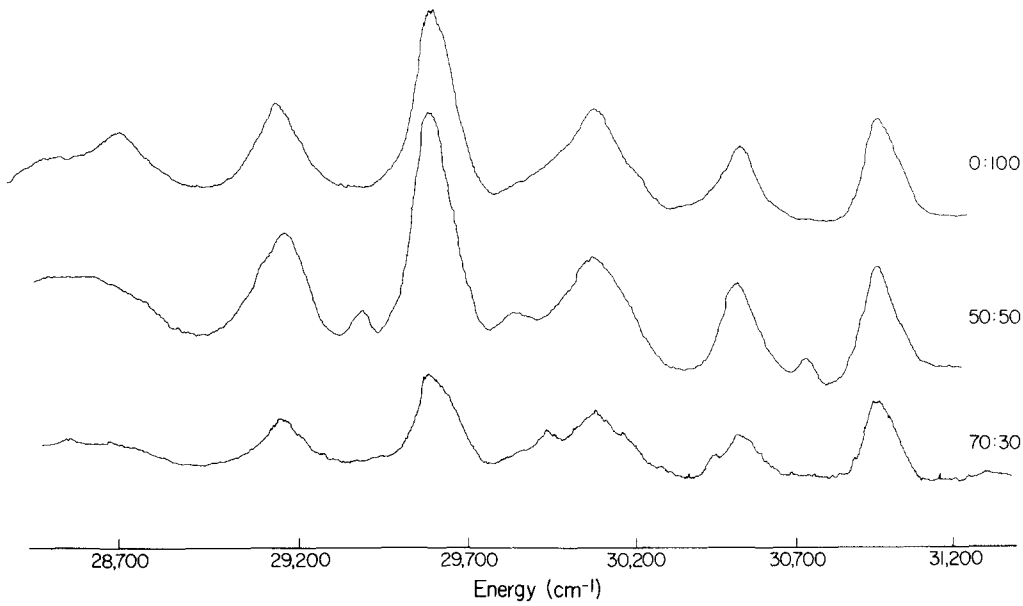

FIG. 12. The fluorescence spectra of naphthalene-h_8 and -βd_1 at 77°K. The ratios correspond to naphthalene-h_8: naphthalene-βd_1 given to the closest 10%(±2%).

another frequency (844 cm^{-1}) to ν_{18} in αd_4. Another alternative assignment more consistent with the results of Mitra and Bernstein would be to correlate the 958-cm^{-1} band with the 937-cm^{-1} band in h_8 and both the 860 and 1395-cm^{-1} bands with the 1383-cm^{-1} band in h_8. However, the intensity distribution seems to rule out this possibility.

The degree of cooperative excitation can be estimated from the intensity ratio of the fluorescence bands belonging to each isotopic modification. Assuming that the transition dipoles are essentially the same, $\mathbf{M}_A \cong \mathbf{M}_B$, we estimate that for 3.5%, 11%, 21%, 28%, and 38% of naphthalene-h_8, the sum of the squares of the excitation amplitudes at naphthalene-h_8 centers are 0.5, 0.6, 0.8, 0.9, and 1.0, respectively.[30] It is interesting to note that, using the experimental density-of-states function, Sommer and Jortner[1b] calculated this quantity for dilute mixed crystals of naphthalene-h_8 in -αd_4 to be ~0.4. It is seen that our estimates are bracketed by this value and unity (in the pure crystal). A theoretical treatment would have to involve, firstly, the identification of the particular configuration that gives the lowest excitation energy and subsequently, the evaluation of excitation amplitudes (i.e., calculating the crystal wavefunction). At the present stage, this has not been possible to do. However, the energy vs concentration plot shows an unmistakable upward bending of the lower Davydov component with decreasing h_8 concentration (Fig. 5). This experimental observation is consistent with the fact that the sum of the squares of the excitation amplitudes at h_8 centers increases faster than linearly with h_8 concentration. (Compare with Fig. 7 where such is not the case.)

Similar to the system discussed in Sec. III.B.2, the emission spectra at 77°K are characterized by large bandwidths and large overlapping of bands. All except the 510- and 1893-cm^{-1} bands are actually composite bands. Nothing can be learned about the degree of cooperative excitation from these data. The shapes of the 510- and 1893-cm^{-1} bands are quite similar to that of the naphthalene-h_8 and -βd_1 system (*vide infra*) except, of course, they shift more drastically with concentration. The theoretical calculations show that the electronic exciton bandwidth of the mixed-crystal system is slightly larger than that of the pure crystal and also that there is a small dip in state density separating the naphthalene-h_8 band from the -αd_4 band. These features cannot be verified experimentally due to uncertainties in measuring the fluorescence intensities. As a consequence, the density-of-states function is found to be very similar in shape to that of the naphthalene-h_8 and -βd_1 system to be discussed in the next section.

4. *Naphthalene-h_8 and Naphthalene-βd_1*

This system is a good example of case (e) in Fig. 8. The vibrational frequencies are practically the same for both napthalene-h_8 and -βd_1. This is supported by the vibrational analysis of naphthalene-βd_1 pure crystal fluorescence. Within the experimental vibronic bandwidth of ~10 cm^{-1} at 4°K, the vibronic spacings

in the emission spectra of h_8 and βd_1 are found to be the same. Thus at 4°K the mixed-crystal spectra show origins that vary with concentration and coincide with the low-energy absorption edge. Furthermore, the vibronic structure shows no change in going from pure naphthalene-h_8 to pure naphthalene-βd_1. These features are also observed in the spectrum of naphthalene-h_8 and -d_8. However, the interpretations are quite different. In the case of h_8 and d_8 no cooperative excitations are observed while here cooperative excitations are expected but cannot be observed because $\epsilon_A{}^{\text{vib}} \cong \epsilon_B{}^{\text{vib}}$. It is worth noting that if no $\mathbf{k}$ mixing occurs, the sum of the squares of excitation amplitudes of a component should be proportional to its concentration. Investigations of other systems[31] with a small energy gap but a large vibrational energy difference would be of great interest in this respect.

Emission spectra at 77°K are shown in Fig. 12. They resemble pure crystal fluorescence in every respect. The origin shifts slightly with concentration with no change in the band shape. Without further elaboration, it should be evident that the density-of-states functions also resemble that of the pure crystal. This not only agrees with the theoretical calculations in I but also indicates that all the deuterated naphthalenes have indeed the same band structure (see also the top band in Fig. 9). Thus the assumption that intermolecular interactions are invariant to isotopic substitution is well justified.

IV. CONCLUSIONS

In this series of investigations, we attempt to answer the following questions: (1) What parameters govern the energy states and optical spectra of heavily doped mixed crystals? (2) How well do we know the values of these parameters? In the theoretical treatment, we illustrate that in the first approximation these parameters are: density-of-states function of the pure crystal, energy gap, and the location of the $\mathbf{k}=\mathbf{0}$ levels. Calculations based on these parameters are found to be in general agreement with experiments except for cluster states important at low guest concentrations and large energy gap. Therefore in a general theory of disordered solids, tractable solutions that account for the pair effects are yet to be sought. As to the second question, the experimental density-of-states function is found to be basically sound. However, more accurate dispersion relations[32] are still needed as well as a better understanding of the quantum mechanical origin of exciton interactions. In the latter aspect, the inadequacy of the octopole model has been demonstrated by several workers.[1,4] Since the present formulation, which is based on a neutral Frenkel exciton model, is generally supported by experimental results, the role of the charge-transfer[33] interaction cannot be a predominant one. The same conclusion was also reached by Hanson *et al.*[1a] and by Sommer and Jortner[1b] in connection with their studies of isolated impurity states. In short, none of the present theories on the origin of exciton interactions seem to be completely satisfactory.

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Absolute Oscillator Strengths for the CH^+, CD^+, and BH $A\ ^1\Pi$–$X\ ^1\Sigma^+$ Transition

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Radiative lifetime measurements for the $CH^+(CD^+)$ $A\ ^1\Pi$ state (70±25 nsec) and for the BH $A\ ^1\Pi$ state (159±16 nsec) are reported. Absolute oscillator strengths are computed using RKR Franck–Condon factors. Astrophysical implications of these data are indicated.

INTRODUCTION

In this laboratory we have obtained radiative lifetimes for many of the first- and second-row hydrides and deuterides, including to date CH,[1] CD,[1] NH,[2,3] OH,[4] SiH, and SiD.[2,3] In the present study, we have measured the radiative lifetime of the lowest excited state for the BH, CH^+, and CD^+ species. These species are especially interesting to astronomy since CH^+ may be formed primarily via diatomic recombination even under interstellar conditions,[5] if among other considerations the oscillator strength is sufficiently large. Since pure CH^+ (or CD^+) $A\ ^1\Pi$–$X\ ^1\Sigma^+$ emission is difficult to obtain unblended with nearby CH emissions at our resolution of 5–8 Å, we have also studied the $A\ ^1\Pi$ state of BH, the isoelectronic species. It is expected that f values for the corresponding transitions in the two molecules would be similar.

EXPERIMENTAL

The phase-shift method applied here has been discussed in detail elsewhere.[6,7] The $A\ ^1\Pi$ states of BH, CH^+, and CD^+ were excited by an rf-modulated beam of 200-V electrons directed into a 10% mixture of diborane in helium, analyzed-grade CH_4 (Matheson), and CD_4 of 99.1% purity (Merck, Sharp and Dohme), respectively. The phase shift between the input excitation and the modulated emission is a direct measure of the radiative lifetime of the upper state being studied, in the absence of competing or additional processes. The NeII 1908–1917-Å multiplet was used as a phase reference since it is known to be cascade free and has a well-defined radiative lifetime.[8] The modulating frequency was varied from 0.54–3.04 MHz to allow separation of overlapping emissions in CH^+ (from CH) and CD^+ (from CD). Checks for lifetime dependence upon electron voltage or parent gas pressure showed no dependence on these parameters.

The observed emission spectrum of BH $A\ ^1\Pi$–$X\ ^1\Sigma^+$ is shown in Fig. 1. The CH and CD emission spectra are identical to those shown by Hesser and Lutz[1] and will not be reproduced here.

In a measurement where two emissions overlap, phase-shift measurements can be made as a function of modulating frequency, as done here. Then the phase angle determined is given by

$$\Phi=\tan^{-1}[(R\omega\tau_1+\omega\tau_2)/(R+1)],$$

where we have taken τ_1 to be the longer-lived species (state), and τ_2, the shorter-lived species (state), and where R is the frequency-dependent amplitude ratio of the two overlapping emissions, as defined by

$$R=(I_2/I_1)[(1+\omega^2\tau_2^2)/(1+\omega^2\tau_1^2)]^2$$

where $(I_2/I_1)^2$ is the instantaneous number density ratio of the two species (states), as would be formed by a pulse excitation at $t=0$.[9] In the case of the CH^+ $A\ ^1\Pi$–$X\ ^1\Sigma^+$ transition, we find overlapping by the very intense CH $A\ ^2\Delta$–$X\ ^2\Pi$ transition. Measurements of the lifetime of the $A\ ^2\Delta$ state of CH (and CD here) were made carefully over the four frequencies 0.54, 0.96, 1.71, and 3.04 MHz. The lifetime of 476±50 nsec was constant over this range of frequencies for the CH $A\ ^2\Delta$ state and was found to be in agreement with the earlier measurements of Hesser and Lutz[1] made at the lower two frequencies. This indicates that only a short-lived cascading of much less than 1% can be affecting